

Structure and Electrochemical Properties of Layered Oxide Films Prepared by Electrophoretic Deposition

M. Koinuma, H. Seki, D. Matsuo, H. Nakashima, and Y. Matsumoto

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

The compounds with layered structure have interesting chemical properties in the fields such as intercalation, photocatalysis, ion-exchange, photoluminescence, and electrochemistry, and their properties largely change with kinds of molecules and/or ions existed in the interlayer. The fixation of the layered compounds on a substrate is very important for practical application. We have demonstrated that the electrophoretic deposition technique is very useful to prepare the films of layered oxides directly from the fine particle suspensions. The electrophoretic deposition technique is well known as a method to prepare various ceramic and colloidal metal films from the suspensions containing their fine particles controlling the film thickness by the electrolysis time and current. However, thus far the electrophoretic deposition technique has not been used for the fixation of the layered compounds onto the substrate. It is also demonstrated in this paper that highly oriented and strongly adhesive films can be obtained accompanying the composition change by the EPD technique.

Nobate and titanate with layered structure are known as typical photocatalysts for an overall decomposition of water into H₂ and O₂. In this report, the electrochemical properties of the layered niobate and titanate oxide film fixed on platinum substrate prepared by electrophoretic deposition were also examined.

Layered potassium niobate (K₄Nb₆O₁₇) and cesium titanate (Cs_xTi_nO_{2n+1}, n=2, 5) were prepared by conventional solid state method. These powders were pulverized in a mortar to form a powder with particle sizes less than about 10 μm. Electrodes were prepared by the electrophoresis in alcohol suspensions containing these powders after ultrasonic wave illumination.

Xe arc lamp was focused on the electrodes through the quartz cell for photoelectrochemical measurement. Cyclic voltammograms were measured with and without long pass filters which had various wavelength areas. The wavelength dependence of the photoelectrochemical current was measured by using the monochrome meter.

The characterization of the deposited films was examined with SEM, XRD, AFM, XPS and UV-VIS reflected measurement.

Figure 1 shows the XRD patterns of cesium titanate (Cs_xTi_{2-x/4}□_{x/4}O₄) films prepared by the electrophoretic deposition in methanol solution, where that of these powders are also shown for comparison. It should be noted that all the deposited films are highly oriented with the b-axis perpendicular to the substrate surface and that the compositions (structures) of the deposited films depend on the type of the electrode (anode or cathode). The types of the electric charge on the particles will complicatedly change by the Cs⁺ exchange by H⁺, and/or adsorption of H⁺ in the methanol solution. Anyhow, the electric charge density on the cleavage

surface (0n0) of the particles will be higher than the other surfaces. This will be the main reason for the highly orientated deposition of the layered oxides. The present EPD model for the H-T sample is illustrated in Figure 2.

Figure 3 shows the XRD patterns of the electrophoretic deposited K₄Nb₆O₁₇ films. The depositions occurred at both the anode and cathode in ethanol solution. The amounts of the deposits at the anode were much larger than those at the cathode. The deposited films at the anode and the cathode were anhydrite form (K₄Nb₆O₁₇) and hydrate form (K₄Nb₆O₁₇•3H₂O), respectively. The hydrated particles will be charged positively by the H⁺ adsorption in the solution immediately after the immersion into the solution. On the other hand, the particles will be charged negatively by dissociation of some K⁺ ions from the particles in the solution, leading to the deposition at the anode. Consequently, both type particles charged with positive and negative exist in the solution. The reason why the anodic deposited film was the anhydrite form is because water molecules between the NbO₆ layers decomposed by photooxidation.

Properties of the oxide films prepared by the electrophoretic deposition is being examined at present.

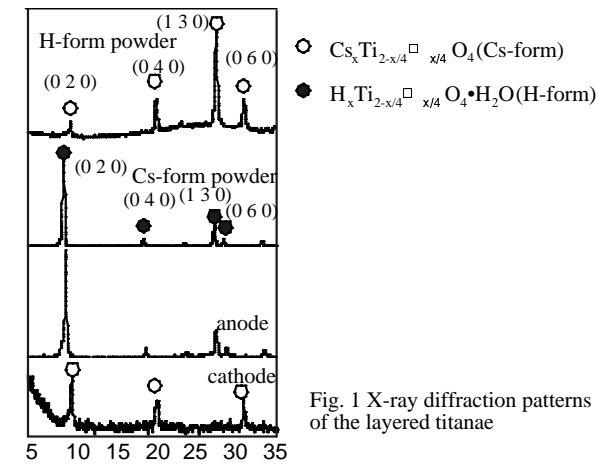


Fig. 1 X-ray diffraction patterns of the layered titanate

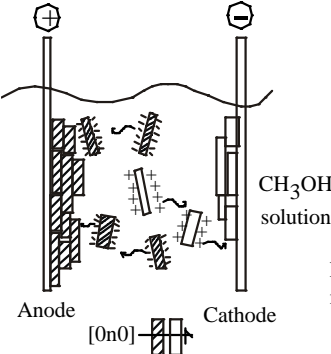


Fig.2 Electrophoretic deposition model of the layered compound.

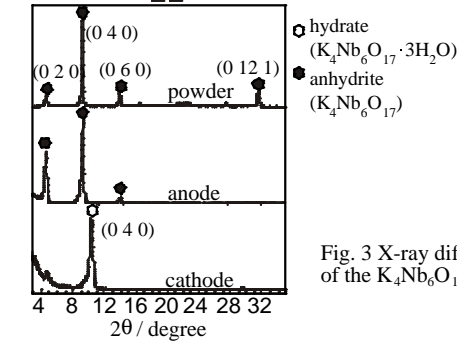


Fig. 3 X-ray diffraction patterns of the K₄Nb₆O₁₇ samples.